Designation: E 202 – 05

Standard Test Methods for Analysis of Ethylene Glycols and Propylene Glycols[1]

This standard is issued under the fixed designation E 202; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the chemical and physical analysis of the commonly available grades of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, and dipropylene glycol. The key sections appear in the following order:

	Sections
Purity of Reagents	4
Specific Gravity	6-8
Distillation Range	9-11
Acidity	12-14
Water	15-17
Iron	18-26
Color	27-29
Gas Chromatographic Analysis	30-40

1.2 Review the current appropriate Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 891 Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals

D 1078 Test Method for Distillation Range of Volatile Organic Liquids

D 1193 Specification for Reagent Water

D 1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)

D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter

D 5386 Test Method for Color of Liquids Using Tristimulus Colorimetry

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E 203 Test Method for Water Using Karl Fischer Reagent

E 394 Test Method for Iron in Trace Quantities Using the 1,10-Phenanthroline Method

E 611 Test Methods for Low Concentrations of Diethylene Glycol in Ethylene Glycol by Gas Chromatography

E 1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

E 1615 Test Method for Iron in Trace Quantities Using the FerroZine Method

E 2409 Test Method for Glycol Impurities in Mono-, Di-, Tri-, and Tetraethylene Glycol (Gas Chromatographic Method)

3. Significance and Use

3.1 These test methods measure certain chemical and physical properties of ethylene glycols and propylene glycols and may be used to determine compliance with specification in which limits are established for these properties. For those tests that use the procedure of another ASTM test method, that test method should be consulted for additional information on the significance and use of that test.

3.2 Alternative test methods and technology for several of the methods can be found in the Appendix. The alternative test methods do not have precision data for the application of these

[1] These test methods are under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and are the direct responsibility of Subcommittee E15.01 on General Standards.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

methods in analyzing glycols. Use of these methods is optional and individuals using the alternative methods should assure themselves that the method is sufficiently precise. Precision data presented is only for the original test methods listed.

4. Purity of Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II or III.

5. Quality Control

5.1 It is recommended that a control chart for the concentration of the impurities in the glycol quality control sample be established and maintained according to common guidelines.[4] Measure the control sample each time a test sample(s) is tested. If the measured value exceeds the action limit of the control chart, take appropriate action before proceeding with sample tests.

SPECIFIC GRAVITY

6. Procedure

6.1 Determine the relative density of the sample at 20/20°C using the pycnometer test method in accordance with Test Methods D 891, except determine the water and sample weights of the pycnometer at 20.0 ± 0.1°C.

7. Report

7.1 Report the relative density at 20/20°C (in air) to the nearest 0.0001 unit.

8. Precision and Bias

8.1 The following criteria should be used for judging the acceptability of results (see Note 1):

8.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0000651 unit at 96 dF. The 95 % limit for the difference between two such runs is 0.0002 unit.

8.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0000598 units at 48 df. The 95 % limit for the difference between two such averages is 0.0002 unit.

8.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.000191 unit at 5 dF. The 95 % limit for the difference between two such averages is 0.0005 unit.

NOTE 1—These precision estimates are based on interlaboratory studies performed in 1962 and 1963 on six samples of the five glycols whose specific gravity values range from approximately 1.0233 to 1.1255. A total of ten laboratories cooperated in the studies in which each analyst performed duplicate determinations on each sample on each of two days.[5] Practice E 180 was used in developing these precision estimates.

8.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

DISTILLATION RANGE

9. Procedure

9.1 Determine the distillation range of the sample in accordance with Test Method D 1078. Use the conditions as specified in Test Method D 1078, and the ASTM Solvents Distillation Thermometer shown in Table 1. (See Note 2 for certain allowable exceptions in applying this test method to triethylene glycol.)

NOTE 2—In the distillation of triethylene glycol, it may not be possible to collect the first drop of liquid within 15 min or to maintain the prescribed distillation rate of 4 to 5 mL/min with some sources of gas. In this case, up to 30 min can be allowed to collect the first drop, and a distillation rate of 2 to 3 mL/min is satisfactory. Alternatively, the flask chamber may be covered with a suitable shield so that only the upper neck and thermometer are exposed to room air to achieve the specified rates.

9.2 Use the following values of *K* in the equation for barometric correction (Test Method D 1078):

Chemical	*K*
Ethylene glycol	0.045
Diethylene glycol	0.050
Triethylene glycol	0.055
Propylene glycol	0.043
Dipropylene glycol	0.051

10. Report

10.1 Report the corrected temperatures to the nearest 0.1°C at each volume required by the specification for the glycol being analyzed.

[3] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* VWR International Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[4] ASTM Manual on Presentation of Data and Control Chart Analysis, 7th Edition, ASTM Manual Series MNL 7A (revision of Special Technical Publication (STP) 15D).

[5] Details of the interlaboratory study are available as Research Report E15-0013 from ASTM Headquarters.

TABLE 1 Thermometers for Distillation Range

Glycol	Thermometer Number	Thermometer Range
Ethylene glycol	104C	173 to 227°C
Diethylene glycol	106C	223 to 277°C
Triethylene glycol	107C	248 to 302°C
Propylene glycol	104C	173 to 227°C
Dipropylene glycol	106C	223 to 277°C

11. Precision and Bias

11.1 The following criteria should be used for judging the acceptability of results (Note 3):

11.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the value in the table.

11.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

11.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value in the table.

TABLE 2 Distillation Range Precision Values

	Ethylene Glycol Distillation Range		Diethylene and Triethylene Glycols	Propylene and Dipropylene Glycols
	0 to 5°C/qa	5 to 15°C		
Initial boiling point,° C:				
Repeatability				
Standard deviation	0.154 (54[A])	0.154 (54)	0.218 (52)	0.148 (56)
95 % limit	0.4	0.4	0.6	0.4
Laboratory Precision (Within Laboratory Between Days)				
Standard deviation	0.173 (27)	0.173 (27)	0.119 (23)	0.0901(28)
95 % limit	0.5	0.5	0.4	0.2
Reproducibility				
Standard deviation	0.414 (8)	0.414 (8)	0.489 (6)	0.190 (6)
95 % limit	1.2	1.2	1.4	0.5
5 mL, °C:				
Repeatability				
Standard deviation	0.118 (54)	0.118 (54)	...	...
95 % limit	0.3	0.3	...	...
Laboratory Precision (Within Laboratory Between Days)				
Standard deviation	0.147 (27)	0.147 (27)	...	...
95 % limit	0.4	0.4	...	...
Reproducibility				
Standard deviation	0.317 (8)	0.317 (8)	...	...
95 % limit	0.9	0.9	...	...
50 mL, °C:				
Repeatability				
Standard deviation	0.0783 (54)	0.0783(54)	0.129 (52)	0.0892(56)
95 % limit	0.2	0.2	0.4	0.2
Laboratory Precision (Within Laboratory Between Days)				
Standard deviation	0.0981 (27)	0.0981(27)	0.0961(26)	0.0505(28)
95 % limit	0.3	0.3	0.3	0.1
Reproducibility				
Standard deviation	0.279 (8)	0.279 (8)	0.201 (6)	0.133 (6)
95 % limit	0.8	0.8	0.6	0.4
95 mL, °C:				
Repeatability				
Standard deviation	0.0837 (54)	0.0837(54)	...	...
95 % limit	0.2	0.2	...	...
Laboratory Precision (Within Laboratory Between Days)				
Standard deviation	0.126 (27)	0.126 (27)	...	...
95 % limit	0.4	0.4	...	...
Reproducibility				
Standard deviation	0.336 (8)	0.336 (8)	...	...
95 % limit	0.9	0.9	...	...
Dry point C:				
Repeatability				
Standard deviation	0.0779 (14)	0.384 (36)	0.272 (46)	0.193 (56)
95 % limit	0.2	1.1	0.8	0.5
Laboratory Precision (Within Laboratory Between Days)				
Standard deviation	0.122 (8)	0.640 (18)	0.103 (23)	0.250 (28)
95 % limit	0.3	1.8	0.3	0.7
Reproducibility				
Standard deviation	0.466 (7)	2.77 (8)	1.12 (5)	0.896 (6)
95 % limit	1.3	7.8	3.1	2.5

[A]Degrees of freedom indicated by values within parentheses.

NOTE 3—These precision estimates are based on interlaboratory studies performed in 1962 and 1963 on eleven samples of the five glycols whose distillation ranges varied from 1.4 to 9.7°C. A total of ten laboratories cooperated in the studies in which each analyst performed duplicate determinations on each sample on each of two days.[5] Practice E 180 was used in developing these precision estimates.

11.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

ACIDITY

12. Procedure

12.1 Determine the acidity of the sample in accordance with Test Method D 1613.

13. Report

13.1 Report the acidity, expressed as mass percent of acetic acid, to the nearest 0.0001 %.

14. Precision and Bias

14.1 The following criteria should be used for judging the acceptability of results (see Note 4):

14.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0000918 % absolute at 92 dF. The 95 % limit for the difference between two such runs is 0.0003 % absolute.

14.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.000116 % absolute at 46 dF. The 95 % limit for the difference between two such averages is 0.0003 % absolute.

14.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.000279 % absolute at 5 df. The 95 % limit for the difference between two such averages is 0.0008 % absolute.

NOTE 4—These precision estimates are based on an interlaboratory study performed in 1962 and 1963 on six samples of the five glycols whose acidity values ranged from 0.0008 to 0.0044 %. A total of ten laboratories cooperated in the studies in which each analyst performed duplicate determinations on each of two days.[5] Practice E 180 was used in developing these precision estimates.